Utilization of potassium carbonate for the synthesis of 2-(organylsulfonyl)thieno[2,3-*b*]pyridine derivatives*

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A novel preparative method for the synthesis of 2-(organylsulfonyl)thieno[2,3-*b*]pyridine derivatives has been developed, which allows one to obtain the desired products in a good yield and to shorten the reaction duration. The reaction of 3-cyanopyridine-2(1*H*)-thiones with chloromethyl organyl sulfones in the presence of potassium carbonate as the base gave 2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-amines. The same reaction of methyl 4,6-dimethylpyridine-2(1*H*)-thione-3-carboxylate with chloromethyl organyl sulfones resulted in tautomeric mixtures of 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-oles and 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-ones.

Key words: 3-cyanopyridine-2(1*H*)-thiones, methyl 4,6-dimethylpyridine-2(1*H*)-thione-3-carboxylate, chloromethyl organyl sulfones, potassium carbonate, 2-(organylsulfonyl)-thieno[2,3-*b*]pyridine-3-amines, 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-oles, 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-ones.

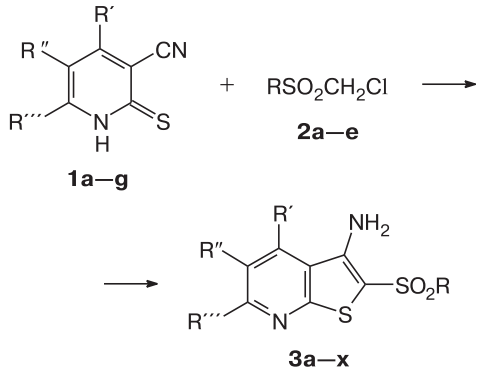
Derivatives of 2-(organylsulfonyl)thieno[2,3-*b*]pyridines are of interest as pharmacological agents. In particular, 3-aryl-2-(organylsulfonyl)thieno[2,3-*b*]pyridines have demonstrated an activity towards the glutamate receptors mGluRl and mGluR5 and can thus be utilized for the treatment of a wide range of neurological and mental diseases.[1,2]

We have previously obtained the first representatives of this class of compounds, 2-(organylsulfonyl)thieno-[2,3-*b*]pyridine-3-amines, *via* the reaction of substituted 3-cyanopyridine-2-thiones and chloromethyl organyl sulfones in DMF in the presence of triethylamine as the base.[3] This reaction at 100—110 °C is usually completed within 7 h. The drawback of that method is the long reaction duration. At this end, we have selected anhydrous potassium carbonate as the base.

Results and Discussion

In the present work, we have utilized 3-cyanopyridin-2(1*H*)-thiones **1a**—**g** bearing alkyl, aryl, trifluoromethyl, amide, acetyl, and ester groups and chloromethyl organyl sulfones **2a**—**c**, wherein the organyl group is phenyl, benzyl, and butyl ones, and also chloromethylsulfonamides **2d**,**e**. The reaction was carried out in DMF at a molar ratio of reagents **1** : **2** : K_2CO_3 equal to 1 : 1 : 1.4 at 70—75 °C for 40—50 min (Scheme 1). The yields of compounds **3a**—**x** are given in Table 1.

Scheme 1



Reagents and conditions: K_2CO_3, DMF, 70—75 °C, 50 min.

1	R′	R″ R″R‴	R‴
a	Me	H	Me
b	H	$(CH_2)_4$	
c	Ph	H	Ph
d	CF_3	H	Ph
e	Ph	C(O)NHPh	Me
f	H	Ac	Me
g	Ph	CO_2Et	Me

2: R = Ph (**a**), Bn (**b**), Bu (**c**), morpholin-4-yl (**d**), NHPh (**e**)

* Dedicated to Corresponding Member of the Russian Academy of Sciences G. I. Nikishin on the occasion of his 90th birthday.

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Table 1. Yields of compounds **3a**—**x**

Product	R	R′	R″	R″R‴	R‴	Yield (%)
3a	Ph	Me	H		Me	78
3b	Ph	H		$(CH_2)_4$		70
3c	Ph	Ph	H		Ph	74
3d	Ph	CF_3	H		Ph	69
3e	Ph	Ph	C(O)NHPh		Me	47
3f	Ph	H	Ac		Me	70
3g	Ph	Ph	CO_2Et		Me	55
3h	Bn	Me	H		Me	55
3i	Bn	H		$(CH_2)_4$		72
3j	Bn	Ph	H		Ph	57
3k	Bn	CF_3	H		Ph	31
3l	Bn	Ph	C(O)NHPh		Me	43
3m	Bn	H	Ac		Me	41
3n	Bu	Me	H		Me	74
3o	Bu	H		$(CH_2)_4$		71
3p	Bu	Ph	H		Ph	64
3q	Bu	CF_3	H		Ph	57
3r	Bu	Ph	C(O)NHPh		Me	68
3s	Bu	H	Ac		Me	58
3t	Bu	Ph	CO_2Et		Me	52
3u	Morpholin-4-yl	Me	H		Me	46
3v	Morpholin-4-yl	Ph	H		Ph	44
3w	NHPh	Me	H		Me	36
3x	NHPh	Ph	H		Ph	32

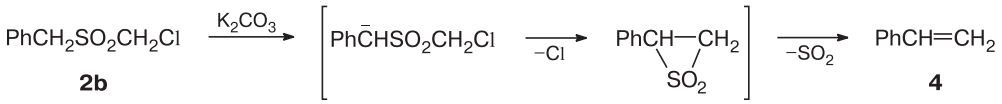
As one can see from Table 1, the yield of desired products **3** depends on the structure of pyridinethione **1** and, especially, on that of sulfone **2**. Thus, the highest yields of the target products were observed for reactions with chloromethyl phenyl sulfone (**2a**, R = Ph), while the lowest ones were in the case of chloromethyl benzyl sulfone (**2b**, R = Bn). The yields of the desired products for reactions with chloromethyl butyl sulfone (**2c**, R = Bu) were intermediate. This can be explained by side reactions proceeding along with the formation of thienopyridines **3** in the case of sulfones **2b** and **2c**. Thus, the interaction of pyridinethione **1** with sulfone **2b** in addition to target products **3h**—**m** provided some amounts of styrene **4**, which was formed *via* the Ramberg—Bäcklund reaction (Scheme 2).

We have also explored the opportunity to obtain thieno[2,3-*b*]pyridines **3** using chloromethylsulfonamides **2d**,**e** as the starting compounds, which can be easily prepared *via* the reaction of chloromethylsulfonyl chloride with amines. The reaction was carried out under the same conditions as in the case of sulfones **2a**—**c** (see Scheme 1). It was found that desired products **3u**—**x** were also produced in this case, but in the yields lower than that for sulfones **2a**—**c** (see Table 1).

It was interesting to investigate the synthetic opportunity for 2-(organylsulfonyl)thieno[2,3-*b*]pyridine derivatives using methyl 4,6-dimethylpyridine-2(1*H*)-thione-3-carboxylate **5** as the starting compound containing the ester group at position 3. Such studies have not been previously conducted. The reaction of compound **5** with sulfones **2a**—**e** was carried out under similar conditions as described above, except that the reaction products were isolated after the acidification of reaction mixture with acetic acid (Scheme 3).

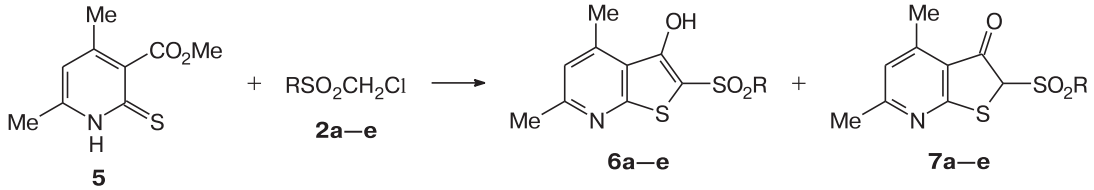
It was found that the products in the reaction of pyridinethione **5** with sulfones **2a**—**e** were mixtures of tautomeric compounds: 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-oles **6a**—**e** and 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-ones **7a**—**e** (Table 2). This fact was confirmed by the presence of absorption bands at 3396—3320 cm^{-1} for the hydroxyl group of compounds **6a**—**e** and at 1708—1704 cm^{-1} for the carbonyl group of compounds **7a**—**e** in the IR spectra of reaction products. ^1H NMR spectra of the reaction products contain proton signals in the region of δ = 8.9—9.5 from the hydroxyl group of compounds **6a**—**e** and δ = 5.1—5.2 from the H(2) atom at the thieno[2,3-*b*]-

Scheme 2



2b **4**

Scheme 3



5 **2a—e** **6a—e** **7a—e**

Reagents and conditions: K_2CO_3, DMF, 70—75 °C, 50 min.

Table 2. Yields of the products and tautomeric ratios in the reaction of compound **5** with chloromethyl organyl sulfones **2a—e**

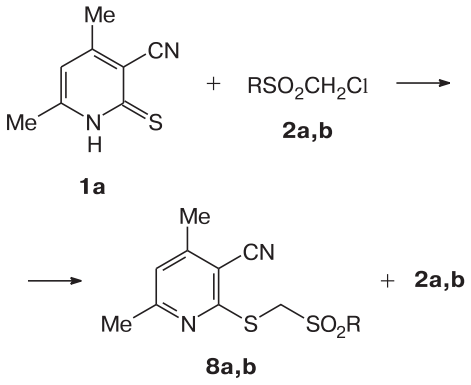
Products	R	Yield (%)	Ratio of tautomers **6** : **7***
6a + **7a**	Ph	51	80 : 20
6b + **7b**	Bn	41	68 : 32
6c + **7c**	Bu	46	83 : 17
6d + **7d**	Morpholin-4-yl	42	90 : 10
6e + **7e**	NHPh	48	40 : 60

* According to the NMR data.

pyridine cycle of compounds **7a—e**. ^{13}C NMR spectra of tautomers **6a—e** contain signals of carbon atoms in the range of δ = 105.70—112.24 from the C(2) atom of thieno[2,3-*b*]pyridine cycle and δ = 145.80—146.17 from the carbon atom bearing the OH group, while those of tautomers **7a—e** contain the signals in the interval of δ = 69.21—70.28 from the C(2) atom of thieno[2,3-*b*]-pyridine cycle and δ = 189.14—190.67 from the carbonyl group. As one can see from Table 2, the major product is tautomer **6** in most reactions, and only in the case of product in the reaction of pyridinethione **5** with sulfone **2e**, tautomer **7e** is the major one.

It was interesting to compare our method for the preparation of 2-(organylsulfonyl)thieno[2,3-*b*]pyridine derivatives with that reported previously in the patent,[1] wherein 2-(arylsulfonyl)thieno[2,3-*b*]pyridine-3-amines were obtained in the yields of 60—80% *via* the reaction of 3-cyanopyridine-2-thione with chloromethyl aryl sulfones in DMF in the presence of sodium methoxide as the base at 120 °C for 2 h. However, in our case, the reaction of 3-cyanopyridine-2(1*H*)-thione **1a** with chloromethyl organyl sulfones **2a,b** in the presence of sodium methoxide under those conditions gave mixtures of starting sulfones **2a**,**b** and alkylation products **8a**,**b** (Scheme 4).

Scheme 4



Reagents and conditions: MeONa, DMF, 120—125 °C, 2 h.

In this case, a quite rare phenomenon was observed since the cation nature affected not only the reaction rate, but also the reaction possibility.

Therefore, we have developed the convenient preparative method for the synthesis of substituted 2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-amines *via* an utilization of potassium carbonate as the base, which allowed us to significantly shorten the reaction time and to obtain the desired products in fairly good yields. It was found that pyridine-2(1*H*)-thione bearing an ester group at the position 3 can also react with chloromethyl organyl sulfones giving the mixture of tautomers, 2-(organylsulfonyl)-thieno[2,3-*b*]pyridine-3-oles and 2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-ones.

Experimental

All values of melting points were measured on a Kofler plate. IR spectra were recorded on a Specord M82 spectrometer in KBr pellets. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker Avance-300 spectrometer in DMSO-d_6 or $CDCl_3$ using $SiMe_4$ as an internal standard. Elemental analysis was carried out using a Perkin-Elmer 2400 CHN analyzer. A chromatographic column loaded with silica gel (60—80 mesh) was used for the isolation of reaction products.

Synthesis of the starting compounds. 3-Cyanopyridine-2(1*H*)-thiones (**1a**)[4], (**1b**)[5], (**1c**)[6], (**1d**)[7], (**1e**)[8], (**1f**)[9], (**1g**)[10] and sulfones (**2a—c**)[3] were prepared according to the known procedures.

Synthesis of chloromethylsulfonamides 2d,e (general procedure). A solution of amine (40 mmol) in $CHCl_3$ (20 mL) was added at 0—5 °C to a solution of chloromethylsulfonyl chloride (3 g, 20 mmol) in $CHCl_3$ (20 mL). The reaction mixture was stirred at that temperature for 20 min, warmed to room temperature, and stirred for 1 h. It was then washed with water (2×30 mL) and dried over $MgSO_4$, the solvent was evaporated, and the product was recrystallized from $CHCl_3$—hexane mixture.

4-(Chloromethylsulfonyl)morpholine (2d). The yield was 3.11 g (78%), colorless crystals, m.p. 69—71 °C (*cf.* Ref. 11: 70.5—71 °C (EtOH)). IR, ν/cm^{-1}: 3016, 2976, 2844, 1456, 1348 (SO_2), 1264, 1160 (SO_2), 1104, 956, 748. ^1H NMR ($CDCl_3$), δ: 3.48 (t, 4 H, CH_2NCH_2, *J* = 4.4 Hz); 3.77 (t, 4 H, CH_2OCH_2, *J* = 4.4 Hz); 4.55 (s, 2 H, CH_2Cl).

1-Chloro-*N*-phenylmethanesulfonamide (2e). The yield was 3.36 g (82%), colorless crystals, m.p. 76—78 °C (*cf.* Ref. 12: 75—78 °C (CCl_4)). IR, ν/cm^{-1}: 3272 (NH), 3004, 2948, 1596, 1486, 1476, 1412, 1364 (SO_2), 1164 (SO_2), 1120, 936, 756, 728, 692. ^1H NMR ($CDCl_3$), δ: 4.50 (s, 2 H, CH_2Cl); 7.02 (br.s, 1 H, NH); 7.24—7.35 (m, 3 H, $H_{Ph}(2)$, $H_{Ph}(4)$, $H_{Ph}(6)$); 7.37—7.46 (m, 2 H, $H_{Ph}(3)$, $H_{Ph}(5)$).

Synthesis of substituted 2-(organylsulfonyl)thieno[2,3-*b*]-pyridines 3a—x (general procedure). Anhydrous K_2CO_3 (0.77 g, 5.6 mmol) was added at 50 °C to a solution of pyridinethione **1a—g** (4 mmol) and sulfone **2a—e** (4 mmol) in DMF (7 mL). The reaction mixture was stirred at 70—75 °C for 50 min, cooled to room temperature, and poured into H_2O (30 mL). The product was extracted with $CHCl_3$ (3×15 mL). The extract was washed with H_2O (3×20 mL) and dried over $MgSO_4$, the solvent was evaporated, and the product was purified by chromatography on silica gel. The eluent was $CHCl_3$—hexane mixture (3 : 2, 2 : 1,

and 3 : 1). After the evaporation of eluate, the substance was recrystallized from an appropriate solvent. During the chromatographic separation of products of the reaction of pyridinethiones **1** and chloromethyl benzyl sulfone **2b**, styrene **4** was found in one of the fractions, whose structure was confirmed by NMR spectroscopy.

4,6-Dimethyl-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3-amine (3a). The yield was 1 g (78%), yellow crystals, m.p. 197—199 °C ($CHCl_3$—MeOH) (*cf.* Ref. 3: m.p. 197—199 °C (MeOH)). Found (%): C, 56.74; H, 4.48; N, 8.63; S, 20.21. $C_{15}H_{14}N_2O_2S_2$. Calculated (%): C, 56.58; H, 4.43; N, 8.80; S, 20.14. IR, ν/cm^{-1}: 3500, 3384 (NH_2), 2916, 1620, 1580, 1552, 1508, 1444, 1300 (SO_2), 1148 (SO_2), 1012, 688. ^{1}H NMR (DMSO-d_6), δ: 2.55 (s, 3 H, 4-CH_3); 2.70 (s, 3 H, 6-CH_3); 5.40 (s, 2 H, NH_2); 6.85 (s, 1 H, $H_{TP}(5)$);* 7.40—7.70 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.92—8.07 (m, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$). ^{13}C NMR (DMSO-d_6), δ: 19.87 (4-CH_3); 23.78 (6-CH_3); 100.95 ($C_{TP}(2)$); 122.39 ($C_{TP}(3a)$); 122.49 ($C_{TP}(5)$); 126.04 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 129.63 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 133.43 ($C_{PhSO_2}(4)$); 142.02 ($C_{PhSO_2}(1)$); 146.00 ($C_{TP}(3)$); 146.29 ($C_{TP}(4)$); 159.87 ($C_{TP}(6)$); 160.11 ($C_{TP}(7a)$).

2-(Phenylsulfonyl)-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-3-amine (3b). The yield was 0.93 g (70%), yellow crystals, m.p. 198—200 °C ($CHCl_3$—MeOH). Found (%): C, 59.44; H, 4.62; N, 8.18; S, 18.48. $C_{17}H_{16}N_2O_2S_2$. Calculated (%): C, 59.28; H, 4.68; N, 8.13; S, 18.62. IR, ν/cm^{-1}: 3448, 3284, 3164 (NH_2), 1632, 1520, 1396, 1304 (SO_2), 1140 (SO_2), 1084, 724. ^{1}H NMR (DMSO-d_6), δ: 1.75—1.95 (m, 4 H, 6,7-CH_{2THTQ});** 2.88 (t, 2 H, 5-CH_{2THTQ}, J = 5.9 Hz); 2.95 (t, 2 H, 8-CH_{2THTQ}, J = 5.9 Hz); 6.85 (s, 2 H, NH_2); 7.50—7.67 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.93 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz); 8.15 (s, 1 H, $H_{THTQ}(4)$). ^{13}C NMR (DMSO-d_6), δ: 22.10 (6-CH_{2THTQ}); 22.26 (7-CH_{2THTQ}); 28.27 (5-CH_{2THTQ}); 32.46 (8-CH_{2THTQ}); 98.64 ($C_{THTQ}(2)$); 123.98 ($C_{THTQ}(3a)$); 125.96 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 129.00 ($C_{THTQ}(4a)$); 129.48 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 131.91 ($C_{THTQ}(4)$); 133.19 ($C_{PhSO2}(4)$); 142.40 ($C_{PhSO_2}(1)$); 144.58 ($C_{THTQ}(3)$); 156.79 ($C_{THTQ}(9a)$); 160.04 ($C_{THTQ}(8a)$).

4,6-Diphenyl-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3-amine (3c). The yield was 1.31 g (74%), yellow crystals, m.p. 213—216 °C ($CHCl_3$—MeOH). Found (%): C, 67.61; H, 4.01; N, 6.28; S, 14.33. $C_{25}H_{18}N_2O_2S_2$. Calculated (%): C, 67.85; H, 4.10; N, 6.33; S, 14.49. IR, ν/cm^{-1}: 3476, 3364 (NH_2), 3060, 1572, 1536, 1512, 1300 (SO_2), 1140 (SO_2), 1084, 748, 720. ^{1}H NMR (DMSO-d_6), δ: 5.46 (s, 2 H, NH_2); 7.45—7.51 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 7.53—7.70 (m, 8 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$, and 4-Ph); 7.76 (s, 1 H, $H_{TP}(5)$); 7.97 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz); 8.12—8.18 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$). ^{13}C NMR (DMSO-d_6), δ: 101.88 ($C_{TP}(2)$); 118.86 ($C_{TP}(5)$); 120.38 ($C_{TP}(3a)$); 126.22 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 127.26 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 128.62 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$); 128.87 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.90 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 129.43 ($C_{4\text{-}Ph}(4)$); 129.62 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 130.15 ($C_{6\text{-}Ph}(4)$); 133.52 ($C_{PhSO_2}(4)$); 135.77 ($C_{4\text{-}Ph}(1)$); 136.92 ($C_{6\text{-}Ph}(1)$); 141.70 ($C_{PhSO_2}(1)$); 144.02 ($C_{TP}(3)$); 148.69 ($C_{TP}(4)$); 156.49 ($C_{TP}(6)$); 160.85 ($C_{TP}(7a)$).

2-(Phenylsulfonyl)-6-phenyl-4-(trifluoromethyl)thieno[2,3-*b*]-pyridine-3-amine (3d). The yield was 1.2 g (69%), yellow crystals, m.p. 260—262 °C ($CHCl_3$—MeOH). Found (%): C, 55.71; H, 3.09; N, 6.39; S, 14.63. $C_{20}H_{13}F_3N_2O_2S_2$. Calculated (%): C, 55.29; H, 3.02; N, 6.45; S, 14.76. IR, ν/cm^{-1}: 3520, 3392 (NH_2), 1632, 1516, 1368, 1304, 1296 (SO_2), 1260, 1172, 1140 (SO_2), 1088, 776, 724, 688. ^{1}H NMR (DMSO-d_6), δ: 6.12 (s, 2 H, NH_2); 7.53—7.58 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.61—7.77 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 8.04 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz); 8.20—8.27 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$); 8.32 (s, 1 H, $H_{TP}(5)$). ^{13}C NMR (DMSO-d_6), δ: 104.37 ($C_{TP}(2)$); 114.42 (q, $C_{TP}(5)$, J = 6.6 Hz); 119.14 (q, CF_3, $J_{C,F}$ = 223.4 Hz); 124.22 ($C_{TP}(3a)$); 126.35 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 127.38 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 128.91 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$); 129.83 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 130.79 ($C_{6\text{-}Ph}(4)$); 132.94 (q, $C_{TP}(4)$, J = 33.2 Hz); 134.02 ($C_{PhSO_2}(4)$); 135.86 ($C_{6\text{-}Ph}(1)$); 140.56 ($C_{PhSO_2}(1)$); 142.02 ($C_{TP}(3)$); 157.36 ($C_{TP}(6)$); 161.82 ($C_{TP}(7a)$).

6-Methyl-4-phenyl-5-(phenylaminocarbonyl)-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3-amine (3e). The yield was 0.94 g (47%), light yellow crystals, m.p. 293—295 °C ($CHCl_3$—MeOH). Found (%): C, 65.04; H, 4.13; N, 8.35; S, 12.72. $C_{27}H_{21}N_3O_3S_2$. Calculated (%): C, 64.91; H, 4.24; N, 8.41; S, 12.83. IR, ν/cm^{-1}: 3492, 3388 (NH_2), 3324 (CONH), 3056, 1676 (C=O), 1608, 1596, 1544, 1444, 1316, 1288 (SO_2), 1144 (SO_2), 760, 688. ^{1}H NMR (DMSO-d_6), δ: 2.63 (s, 3 H, 6-CH_3); 5.23 (s, 2 H, NH_2); 7.04 (t, 1 H, $H_{PhN}(4)$, J = 7.3 Hz); 7.23 (t, 2 H, $H_{PhN}(3)$, $H_{PhN}(5)$, J = 7.3 Hz); 7.28 (d, 2 H, $H_{PhN}(2)$, $H_{PhN}(6)$, J = 7.3 Hz); 7.40—7.52 (m, 5 H, 4-Ph); 7.55—7.68 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.93 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz); 10.33 (s, 1 H, NHCO). ^{13}C NMR (DMSO-d_6), δ: 22.42 (6-CH_3); 101.60 ($C_{TP}(2)$); 119.60 ($C_{PhN}(2)$, $C_{PhN}(6)$); 123.97 ($C_{PhN}(4)$); 126.06 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 126.12 ($C_{TP}(3a)$); 128.45 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.54 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 128.62 ($C_{PhN}(3)$, $C_{PhN}(5)$); 129.44 ($C_{4\text{-}Ph}(4)$); 129.56 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 130.83 ($C_{TP}(5)$); 132.58 ($C_{PhN}(1)$); 133.51 ($C_{PhSO_2}(4)$); 138.03 ($C_{4\text{-}Ph}(1)$); 141.62 ($C_{PhSO_2}(1)$); 144.19 ($C_{TP}(3)$); 144.23 ($C_{TP}(4)$); 155.95 ($C_{TP}(6)$); 159.51 ($C_{TP}(7a)$); 164.29 (C=O).

5-Acetyl-6-methyl-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3-amine (3f). The yield was 0.97 g (70%), yellow crystals, m.p. 195—197 °C ($CHCl_3$—MeOH). Found (%): C, 55.24; H, 4.13; N, 8.01; S, 18.40. $C_{16}H_{14}N_2O_3S_2$. Calculated (%): C, 55.47; H, 4.07; N, 8.09; S, 18.51. IR, ν/cm^{-1}: 3492, 3384 (NH_2), 3068, 1616 (C=O), 1580, 1552, 1444, 1300 (SO_2), 1288, 1148 (SO_2), 1124, 1080, 724. ^{1}H NMR (DMSO-d_6), δ: 2.47 (s, 3 H, 6-CH_3); 2.67 (s, 3 H, $CH_3C(O)$); 6.32 (s, 2 H, NH_2); 7.08 (s, 1 H, $H_{TP}(4)$); 7.58—7.70 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.97 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz). ^{13}C NMR (DMSO-d_6), δ: 19.66 (6-CH_3); 23.75 ($\underline{C}H_3CO$); 100.94 ($C_{TP}(2)$); 122.34 ($C_{TP}(3a)$); 122.41 ($C_{TP}(4)$); 126.02 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 129.58 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$); 133.38 ($C_{PhSO_2}(4)$); 142.01 ($C_{PhSO_2}(1)$); 145.92 ($C_{TP}(3)$); 146.25 ($C_{TP}(5)$); 159.80 ($C_{TP}(6)$); 160.09 ($C_{TP}(7a)$); 193.47 ($CH_3\underline{C}O$).

Ethyl 3-amino-6-methyl-4-phenyl-2-(phenylsulfonyl)thieno-[2,3-*b*]pyridine-5-carboxylate (3g). The yield was 1 g (55%), yellowish white crystals, m.p. 170—171 °C ($CHCl_3$—MeOH). Found (%): C, 61.19; H, 4.33; N, 6.08; S, 14.27. $C_{23}H_{20}N_2O_4S_2$. Calculated (%): C, 61.04; H, 4.45; N, 6.19; S, 14.19. IR, ν/cm^{-1}: 3496, 3388 (NH_2), 3068, 2968, 1728 (C=O), 1604, 1548, 1308 (SO_2), 1288, 1144 (SO_2). ^{1}H NMR (DMSO-d_6), δ: 0.82 (t, 3 H, $C\underline{H}_3CH_2O$, J = 7.3 Hz); 2.57 (s, 3 H, 6-CH_3); 3.93 (q, 2 H, $CH_3C\underline{H}_2O$, J = 7.3 Hz); 5.26 (s, 2 H, NH_2); 7.47 (d, 2 H, $H_{4\text{-}Ph}(2)$, $H_{4\text{-}Ph}(6)$, J = 7.3 Hz); 7.50—7.70 (m, 6 H, $H_{4\text{-}Ph}(3)$, $H_{4\text{-}Ph}(4)$, $H_{4\text{-}Ph}(5)$, and $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.93 (d, 2 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 8.1 Hz). ^{13}C NMR (DMSO-d_6), δ: 13.31 ($\underline{C}H_3CH_2O$); 22.70 (6-CH_3); 61.24 ($CH_3\underline{C}H_2O$); 101.81 ($C_{TP}(2)$); 119.39 ($C_{TP}(3a)$); 126.22 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$); 127.03

* TP is the thienopyridine moiety.

** THTQ is the tetrahydrothienoquinoline moiety.

(C_{TP}(5)); 128.47 ($C_{4\text{-}Ph}$(3), $C_{4\text{-}Ph}$(5)); 128.67 ($C_{4\text{-}Ph}$(2), $C_{4\text{-}Ph}$(6)); 129.64 (C_{PhSO_2}(2), C_{PhSO_2}(6)); 129.67 ($C_{4\text{-}Ph}$(4)); 132.71 ($C_{4\text{-}Ph}$(1)); 133.59 (C_{PhSO_2}(4)); 141.52 (C_{PhSO_2}(1)); 144.10 (C_{TP}(3)); 144.97 (C_{TP}(4)); 155.65 (C_{TP}(6)); 160.14 (C_{TP}(7a)); 166.46 (C=O).

2-(Benzylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3-amine (3h). The yield was 0.73 g (55%), yellow crystals, m.p. 182—184 °C ($CHCl_3$—MeOH). Found (%): C, 57.61; H, 4.93; S, 19.21. $C_{16}H_{16}N_2O_2S_2$. Calculated (%): C, 57.81; H, 4.85; S, 19.29. IR, ν/cm^{-1}: 3484, 3368 (NH_2), 1320 (SO_2), 1144 (SO_2). ^{1}H NMR (DMSO-d_6), δ: 2.48 (s, 3 H, 4-CH_3); 2.63 (s, 3 H, 6-CH_3); 4.62 (s, 2 H, CH_2SO_2); 5.94 (s, 2 H, NH_2); 7.06 (s, 1 H, H_{TP}(5)); 7.20—7.40 (m, 5 H, $CH_2\underline{Ph}$). ^{13}C NMR (DMSO-d_6), δ: 19.66 (4-CH_3); 23.74 (6-CH_3); 61.28 (Ph$\underline{C}H_2$); 99.54 (C_{TP}(2)); 122.04 (C_{TP}(3a)); 122.26 (C_{TP}(5)); 128.15 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.37 (C_{BnSO_2}(4)); 128.64 (C_{BnSO_2}(1)); 130.85 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 145.60 (C_{TP}(3)); 146.92 (C_{TP}(4)); 159.59 (C_{TP}(6)); 160.04 (C_{TP}(7a)).

2-(Benzylsulfonyl)-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-3-amine (3i). The yield was 1.03 g (72%), yellow crystals, m.p. 201—203 °C ($CHCl_3$—MeOH). Found (%): C, 60.18; H, 5.00; N, 7.90; S, 18.14. $C_{18}H_{18}N_2O_2S_2$. Calculated (%): C, 60.31; H, 5.06; N, 7.81; S, 17.89. IR, ν/cm^{-1}: 3448, 3304 (NH_2), 3176, 2932, 2864, 1632, 1560, 1396, 1300 (SO_2), 1140 (SO_2), 1112, 796, 696. ^{1}H NMR (DMSO-d_6), δ: 1.80—2.00 (m, 4 H, 6,7-CH_{2THTQ}); 2.88 (t, 2 H, 5-CH_{2THTQ}, J = 5.9 Hz); 2.98 (t, 2 H, 8-CH_{2THTQ}, J = 5.9 Hz); 4.40 (s, 2 H, CH_2SO_2); 4.92 (s, 2 H, NH_2); 7.17—7.33 (m, 5 H, $CH_2\underline{Ph}$); 7.48 (s, 1 H, H_{THTQ}(4)). ^{13}C NMR (DMSO-d_6), δ: 22.14 (6-CH_{2THTQ}); 22.30 (7-CH_{2THTQ}); 28.30 (5-CH_{2THTQ}); 32.49 (8-CH_{2THTQ}); 61.25 (Ph$\underline{C}H_2$); 96.37 (C_{THTQ}(2)); 123.73 (C_{THTQ}(3a)); 128.20 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.38 (C_{BnSO_2}(4)); 128.85 (C_{THTQ}(4a)); 128.93 (C_{BnSO_2}(1)); 130.86 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 131.70 (C_{THTQ}(4)); 145.22 (C_{THTQ}(3)); 156.72 (C_{THTQ}(9a)); 159.90 (C_{THTQ}(8a)).

2-(Benzylsulfonyl)-4,6-diphenylthieno[2,3-*b*]pyridine-3-amine (3j). The yield was 1.04 g (57%), light yellow crystals, m.p. 214—216 °C ($CHCl_3$—MeOH). Found (%): C, 68.28; H, 4.50; N, 6.23; S, 14.33. $C_{26}H_{20}N_2O_2S_2$. Calculated (%): C, 68.40; H, 4.42; N, 6.14; S, 14.05. IR, ν/cm^{-1}: 3496, 3384 (NH_2), 3060, 2968, 2920, 1608, 1572, 1536, 1388, 1304 (SO_2), 1140 (SO_2), 1116, 876, 796, 756, 712. ^{1}H NMR (DMSO-d_6), δ: 4.63 (s, 2 H, CH_2SO_2); 5.03 (s, 2 H, NH_2); 7.18—7.32 (m, 5 H, $CH_2\underline{Ph}$); 7.48—7.57 (m, 5 H, 4-Ph); 7.59—7.68 (m, 3 H, $H_{6\text{-}Ph}$(3), $H_{6\text{-}Ph}$(4), $H_{6\text{-}Ph}$(5)); 7.83 (s, 1 H, H_{TP}(5)); 8.17—8.25 (m, 2 H, $H_{6\text{-}Ph}$(2), $H_{6\text{-}Ph}$(6)). ^{13}C NMR (DMSO-d_6), δ: 61.25 (Ph$\underline{C}H_2$); 99.33 (C_{TP}(2)); 118.78 (C_{TP}(5)); 120.12 (C_{TP}(3a)); 127.36 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.32 (C_{Ph}(3), C_{Ph}(5), C_{Ph}(6)); 128.50 (C_{BnSO_2}(4)); 128.65 ($C_{6\text{-}Ph}$(2), $C_{6\text{-}Ph}$(6)); 128.70 (C_{BnSO_2}(1)); 128.90 ($C_{4\text{-}Ph}$(3), $C_{4\text{-}Ph}$(5)); 128.98 ($C_{4\text{-}Ph}$(2), $C_{4\text{-}Ph}$(6)); 129.49 ($C_{4\text{-}Ph}$(4)); 130.23 ($C_{6\text{-}Ph}$(4)); 131.04 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 135.81 ($C_{4\text{-}Ph}$(1)); 137.04 ($C_{6\text{-}Ph}$(1)); 144.90 (C_{TP}(3)); 148.63 (C_{TP}(4)); 156.48 (C_{TP}(6)); 160.85 (C_{TP}(7a)).

2-(Benzylsulfonyl)-6-phenyl-4-(trifluoromethyl)thieno[2,3-*b*]-pyridine-3-amine (3k). The yield was 0.55 g (31%), yellow crystals, m.p. 210—212 °C ($CHCl_3$—MeOH). Found (%): C, 56.43; H, 3.41; N, 6.18; S, 14.22. $C_{21}H_{15}F_3N_2O_2S_2$. Calculated (%): C, 56.24; H, 3.37; N, 6.25; S, 14.30. IR, ν/cm^{-1}: 3484, 3392 (NH_2), 1312 (SO_2), 1140 (SO_2). ^{1}H NMR (DMSO-d_6), δ: 4.75 (s, 2 H, CH_2SO_2); 5.73 (s, 2 H, NH_2); 7.20—7.35 (m, 5 H, $CH_2\underline{Ph}$), 7.55—7.62 (m, 3 H, $H_{6\text{-}Ph}$(3), $H_{6\text{-}Ph}$(4), $H_{6\text{-}Ph}$(5)); 8.22—8.30 (m, 2 H, $H_{6\text{-}Ph}$(2), $H_{6\text{-}Ph}$(6)); 8.33 (s, 1 H, H_{TP}(5)). ^{13}C NMR (DMSO-d_6), δ: 61.27 (Ph$\underline{C}H_2$); 103.76 (C_{TP}(2)); 114.39 (q, C_{TP}(5), J = 6.6 Hz); 119.15 (q, CF_3, $J_{C,F}$ = 226.7 Hz); 124.28 (C_{TP}(3a)); 127.57 ($C_{6\text{-}Ph}$(3), $C_{6\text{-}Ph}$(5)); 128.30 (C_{BnSO_2}(1)); 128.36 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.65 (C_{BnSO_2}(4)); 129.14 ($C_{6\text{-}Ph}$(2), $C_{6\text{-}Ph}$(6)); 130.97 ($C_{6\text{-}Ph}$(4)); 131.00 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 132.98 (q, C_{TP}(4), J = 33.2 Hz); 135.98 ($C_{6\text{-}Ph}$(1)); 143.04 (C_{TP}(3)); 157.31 (C_{TP}(6)); 161.86 (C_{TP}(7a)).

2-(Benzylsulfonyl)-6-methyl-4-phenyl-5-(phenylaminocarbonyl)thieno[2,3-*b*]pyridine-3-amine (3l). The yield was 0.88 g (43%), light yellow crystals, m.p. 296—298 °C ($CHCl_3$—MeOH). Found (%): C, 65.63; H, 4.66; N, 8.24; S, 12.27. $C_{28}H_{23}N_3O_3S_2$. Calculated (%): C, 65.48; H, 4.51; N, 8.18; S, 12.48. IR, ν/cm^{-1}: 3483, 3392, 3322 (NH_2), 1685 (C=O), 1322 (SO_2), 1144 (SO_2). ^{1}H NMR (DMSO-d_6), δ: 2.63 (s, 3 H, 6-CH_3); 4.58 (s, 2 H, CH_2SO_2); 4.73 (s, 2 H, NH_2); 7.02 (t, 1 H, H_{PhN}(4), J = 7.3 Hz); 7.23—7.58 (m, 14 H, H_{PhN}(2), H_{PhN}(3), H_{PhN}(5), H_{PhN}(6), 4-Ph, and $CH_2\underline{Ph}$); 10.34 (s, 1 H, NHCO). ^{13}C NMR (DMSO-d_6), δ: 22.47 (6-CH_3); 61.08 (Ph$\underline{C}H_2$); 100.41 (C_{TP}(2)); 119.61 (C_{PhN}(2), C_{PhN}(6)); 123.98 (C_{PhN}(4)); 126.18 (C_{TP}(3a)); 128.23 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.34 ($C_{4\text{-}Ph}$(3), $C_{4\text{-}Ph}$(5)); 128.45 (C_{BnSO_2}(4)); 128.50 ($C_{4\text{-}Ph}$(2), $C_{4\text{-}Ph}$(6)); 128.64 (C_{PhN}(3), C_{PhN}(5)); 128.67 (C_{BnSO_2}(1)); 129.41 ($C_{4\text{-}Ph}$(4)); 130.65 (C_{TP}(5)); 130.87 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 132.64 (C_{PhN}(1)); 138.09 ($C_{4\text{-}Ph}$(1)); 144.11 (C_{TP}(4)); 144.97 (C_{TP}(3)); 155.76 (C_{TP}(6)); 159.41 (C_{TP}(7a)); 164.40 (C=O).

5-Acetyl-2-(benzylsulfonyl)-6-methylthieno[2,3-*b*]pyridine-3-amine (3m). The yield was 0.59 g (41%), light yellow crystals, m.p. 188—190 °C ($CHCl_3$—MeOH). Found (%): C, 56.82; H, 4.54; N, 7.91; S, 17.66. $C_{17}H_{16}N_2O_3S_2$. Calculated (%): C, 56.65; H, 4.47; N, 7.77; S, 17.79. IR, ν/cm^{-1}: 3444, 3360 (NH_2), 3072, 2908, 1616 (C=O), 1584, 1552, 1296 (SO_2), 1148 (SO_2), 1104, 808. ^{1}H NMR (DMSO-d_6), δ: 2.50 (s, 3 H, 6-CH_3); 2.66 (s, 3 H, CH_3C(O)); 4.61 (s, 2 H, CH_2SO_2); 7.08 (s, 1 H, H_{TP}(4)); 7.20—7.40 (m, 5 H, $CH_2\underline{Ph}$). ^{13}C NMR (DMSO-d_6), δ: 19.75 (6-CH_3); 23.92 ($\underline{C}H_3$CO); 61.35 (Ph$\underline{C}H_2$); 98.25 (C_{TP}(2)); 122.13 (C_{TP}(3a)); 122.36 (C_{TP}(4)); 128.25 (C_{BnSO_2}(3), C_{BnSO_2}(5)); 128.49 (C_{BnSO_2}(4)); 128.71 (C_{BnSO_2}(1)); 130.95 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 145.69 (C_{TP}(3)); 147.01 (C_{TP}(5)); 159.71 (C_{TP}(6)); 160.11 (C_{TP}(7a)); 193.98 ($CH_3\underline{C}O$).

2-(Butylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3-amine (3n). The yield was 0.88 g (74%), yellow crystals, m.p. 105—107 °C ($CHCl_3$—MeOH) (*cf.* Ref. 3: m.p. 105—107 °C (MeOH)). Found (%): C, 52.45; H, 6.12; N, 9.48; S, 21.33. $C_{13}H_{18}N_2O_2S_2$. Calculated (%): C, 52.32; H, 6.08; N, 9.39; S, 21.49. IR, ν/cm^{-1}: 3492, 3380 (NH_2), 2960, 2872, 1612, 1552, 1512, 1456, 1392, 1276 (SO_2), 1144 (SO_2), 1112, 808. ^{1}H NMR (DMSO-d_6), δ: 0.93 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.27—1.40 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.57—1.70 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.55 (s, 3 H, 4-$CH_3$); 2.70 (s, 3 H, 6-$CH_3$); 3.22 (t, 2 H, CH_3CH_2-$CH_2C\underline{H}_2$, J = 7.3 Hz); 5.15 (s, 2 H, NH_2); 6.87 (s, 1 H, H_{TP}(5)). ^{13}C NMR (DMSO-d_6), δ: 13.43 ($\underline{C}H_3CH_2CH_2CH_2$); 19.74 (4-$CH_3$); 20.75 ($CH_3\underline{C}H_2CH_2CH_2$); 23.61 (6-$CH_3$); 24.50 ($CH_3CH_2\underline{C}H_2CH_2$); 55.53 ($CH_3CH_2CH_2\underline{C}H_2$); 99.34 ($C_{TP}$(2)); 122.42 ($C_{TP}$(5)); 122.51 ($C_{TP}$(3a)); 145.78 ($C_{TP}$(3)); 146.45 ($C_{TP}$(4)); 159.65 (C(6) TP); 159.88 (C_{TP}(7a)).

2-(Butylsulfonyl)-5,6,7,8-tetrahydrothieno[2,3-*b*]quinoline-3-amine (3o). The yield was 0.92 g (71%), light yellow crystals, m.p. 228—230 °C (MeOH). Found (%): C, 55.41; H, 6.29; N, 8.75; S, 19.59. $C_{15}H_{20}N_2O_2S_2$. Calculated (%): C, 55.53; H, 6.21; N, 8.63; S, 19.76. IR, ν/cm^{-1}: 3452, 3296 (NH_2), 3158, 2932, 2868, 1632, 1568, 1396, 1296 (SO_2), 1124 (SO_2), 1000, 800. ^{1}H NMR (DMSO-d_6), δ: 0.93 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.27—1.40 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.57—1.70 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 1.73—1.95 (m, 4 H, 6,7-CH_{2THTQ}), 2.88 (t, 2 H, 5-CH_{2THTQ}, J = 5.9 Hz); 2.95 (t, 2 H, 8-CH_{2THTQ},

J = 5.9 Hz); 3.29 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2$, J = 7.3 Hz); 6.77 (s, 2 H, NH_2); 8.26 (s, 1 H, $H_{THTQ}(4)$). ^{13}C NMR (DMSO-d_6), δ: 13.45 ($\underline{C}H_3CH_2CH_2CH_2$); 20.75 ($CH_3\underline{C}H_2CH_2CH_2$); 22.14 (6-$CH_{2THTQ}$); 22.31 (7-$CH_{2THTQ}$); 24.58 ($CH_3CH_2\underline{C}H_2CH_2$); 28.30 (5-$CH_{2THTQ}$); 32.47 (8-$CH_{2THTQ}$); 55.39 ($CH_3CH_2$-$CH_2\underline{C}H_2$); 97.14 ($C_{THTQ}(2)$); 124.06 ($C_{THTQ}(3a)$); 128.88 ($C_{THTQ}(4a)$); 131.74 ($C_{THTQ}(4)$); 144.59 ($C_{THTQ}(3)$); 156.73 ($C_{THTQ}(9a)$); 159.76 ($C_{THTQ}(8a)$).

2-(Butylsulfonyl)-4,6-diphenylthieno[2,3-*b*]pyridine-3-amine (3p). The yield was 1.08 g (64%), yellow crystals, m.p. 127—129 °C ($CHCl_3$—MeOH). Found (%): C, 65.55; H, 5.21; N, 6.70; S, 15.36. $C_{23}H_{22}N_2O_2S_2$. Calculated (%): C, 65.38; H, 5.25; N, 6.63; S, 15.17. IR, ν/cm^{-1}: 3468, 3368 (NH_2), 2964, 2936, 2872, 1608, 1576, 1536, 1510, 1392, 1296, 1116, 768, 708, 692. ^1H NMR (DMSO-d_6), δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.27—1.42 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.60—1.72 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 3.30 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2$, J = 7.3 Hz); 5.30 (s, 2 H, NH_2); 7.48—7.55 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 7.56—7.64 (m, 5 H, 4-Ph); 7.83 (s, 1 H, $H_{TP}(5)$); 8.17—8.24 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$). ^{13}C NMR (DMSO-d_6), δ: 13.42 ($\underline{C}H_3CH_2CH_2CH_2$); 20.76 ($CH_3\underline{C}H_2$-$CH_2CH_2$); 24.38 ($CH_3CH_2\underline{C}H_2CH_2$); 55.25 ($CH_3CH_2CH_2\underline{C}H_2$); 100.50 ($C_{TP}(2)$); 118.83 ($C_{TP}(5)$); 120.54 ($C_{TP}(3a)$); 127.30 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 128.69 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$); 128.88 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.91 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 129.43 ($C_{4\text{-}Ph}(4)$); 130.13 ($C_{6\text{-}Ph}(4)$); 135.92 ($C_{4\text{-}Ph}(1)$); 137.05 ($C_{6\text{-}Ph}(1)$); 144.19 ($C_{TP}(3)$); 148.57 ($C_{TP}(4)$); 156.37 ($C_{TP}(6)$); 160.67 ($C_{TP}(7a)$).

2-(Butylsulfonyl)-6-phenyl-4-(trifluoromethyl)thieno[2,3-*b*]-pyridine-3-amine (3q). The yield was 0.95 g (57%), yellow crystals, m.p. 150—152 °C ($CHCl_3$—MeOH). Found (%): C, 52.34; H, 4.20; N, 6.83; S, 15.22. $C_{18}H_{17}F_3N_2O_2S_2$. Calculated (%): C, 52.16; H, 4.13; N, 6.76; S, 15.47. IR, ν/cm^{-1}: 3516, 3392 (NH_2), 2960, 2872, 1624, 1588, 1512, 1372, 1312, 1296 (SO_2), 1260, 1192, 1168, 1142, 1116 (SO_2), 780, 764. ^1H NMR (DMSO-d_6), δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.30—1.43 (m, 2 H, $CH_3C\underline{H}_2CH_2$-CH_2); 1.60—1.74 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 3.42 (t, 2 H, $CH_3CH_2CH_2C\underline{H}_2$, J = 7.3 Hz); 5.96 (s, 2 H, NH_2); 7.54—7.60 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 8.22—8.30 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$); 8.33 (s, 1 H, $H_{TP}(5)$). ^{13}C NMR (DMSO-d_6), δ: 13.37 ($\underline{C}H_3CH_2CH_2CH_2$); 20.71 ($CH_3\underline{C}H_2CH_2CH_2$); 24.26 ($CH_3CH_2\underline{C}H_2CH_2$); 55.28 ($CH_3CH_2CH_2\underline{C}H_2$); 104.10 ($C_{TP}(2)$); 114.39 (q, $C_{TP}(5)$, J = 6.6 Hz); 119.05 (q, CF_3, $J_{C,F}$ = 225.6 Hz); 124.31 ($C_{TP}(3a)$); 127.53 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 129.11 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$); 130.93 ($C_{6\text{-}Ph}(4)$); 132.93 (q, $C_{TP}(4)$, J = 33.2 Hz); 136.01 ($C_{6\text{-}Ph}(1)$); 142.39 ($C_{TP}(3)$); 157.24 ($C_{TP}(6)$); 161.64 ($C_{TP}(7a)$).

2-(Butylsulfonyl)-6-methyl-4-phenyl-5-(phenylaminocarb-onyl)thieno[2,3-*b*]pyridine-3-amine (3r). The yield was 1.3 g (68%), porcelain crystals, m.p. 262—263 °C ($CHCl_3$—MeOH). Found (%): C, 62.54; H, 5.16; N, 8.62; S, 13.22. $C_{25}H_{25}N_3O_3S_2$. Calculated (%): C, 62.61; H, 5.25; N, 8.76; S, 13.37. IR, ν/cm^{-1}: 3516, 3392 (NH_2), 1312 (SO_2), 1140 (SO_2). ^1H NMR (DMSO-d_6), δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.27—1.41 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.54—1.67 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.62 (s, 3 H, 6-$CH_3$); 3.32 (t, 2 H, CH_3CH_2-$CH_2C\underline{H}_2$, J = 7.3 Hz); 5.06 (s, 2 H, NH_2); 7.04 (t, 1 H, $H_{PhN}(4)$, J = 7.3 Hz); 7.26 (t, 2 H, $H_{PhN}(3)$, $H_{PhN}(5)$, J = 7.3 Hz); 7.32 (d, 2 H, $H_{PhN}(2)$, $H_{PhN}(6)$, J = 7.3 Hz); 7.44—7.54 (m, 5 H, 4-Ph); 10.38 (s, 1 H, NHCO). ^{13}C NMR (DMSO-d_6), δ: 13.44 ($\underline{C}H_3$-$CH_2CH_2CH_2$); 20.69 ($CH_3\underline{C}H_2CH_2CH_2$); 22.45 (6-$CH_3$); 24.43 ($CH_3CH_2\underline{C}H_2CH_2$); 55.05 ($CH_3CH_2CH_2\underline{C}H_2$); 100.12 ($C_{TP}(2)$); 119.64 ($C_{PhN}(2)$, $C_{PhN}(6)$); 124.03 ($C_{PhN}(4)$); 126.13 ($C_{TP}(3a)$); 128.46 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.60 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 128.69 ($C_{PhN}(3)$, $C_{PhN}(5)$); 129.47 ($C_{4\text{-}Ph}(4)$); 130.81 ($C_{TP}(5)$); 132.76 ($C_{PhN}(1)$); 138.11 ($C_{4\text{-}Ph}(1)$); 144.14 ($C_{TP}(4)$); 144.33 ($C_{TP}(3)$); 155.74 ($C_{TP}(6)$); 159.30 ($C_{TP}(7a)$); 164.47 (C=O).

5-Acetyl-2-(butylsulfonyl)-6-methylthieno[2,3-*b*]pyridine-3-amine (3s). The yield was 0.76 g (58%), light yellow crystals, m.p. 108—109 °C ($CHCl_3$—MeOH). Found (%): C, 51.62; H, 5.48; N, 8.67; S, 19.55. $C_{14}H_{18}N_2O_3S_2$. Calculated (%): C, 51.51; H, 5.56; N, 8.58; S, 19.64. IR, ν/cm^{-1}: 3492, 3380 (NH_2), 2956, 1616 (C=O), 1608, 1584, 1552, 1272, 1140 (SO_2), 804. ^1H NMR (DMSO-d_6), δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 1.28—1.42 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.55—1.67 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.50 (s, 3 H, $CH_3C(O)$); 2.72 (s, 3 H, 6-CH_3); 3.30 (t, 2 H, $CH_3CH_2CH_2CH_2\underline{C}H_2$, J = 7.3 Hz); 6.13 (s, 2 H, NH_2); 7.10 (s, 1 H, $H_{TP}(4)$). ^{13}C NMR (DMSO-d_6), δ: 13.39 ($\underline{C}H_3CH_2CH_2CH_2$); 19.72 (6-$CH_3$); 20.75 ($CH_3\underline{C}H_2CH_2CH_2$); 23.78 ($\underline{C}H_3CO$); 24.48 ($CH_3CH_2\underline{C}H_2CH_2$); 55.54 ($CH_3CH_2$-$CH_2\underline{C}H_2$); 99.36 ($C_{TP}(2)$); 122.35 ($C_{TP}(4)$); 122.47 ($C_{TP}(3a)$); 145.69 ($C_{TP}(3)$); 146.42 ($C_{TP}(5)$); 159.59 ($C_{TP}(6)$); 159.87 ($C_{TP}(7a)$); 193.38 ($CH_3\underline{C}O$).

Ethyl 3-amino-2-(butylsulfonyl)-6-methyl-4-phenylthieno-[2,3-*b*]pyridine-5-carboxylate (3t). The yield was 0.9 g (52%), light yellow crystals, m.p. 86—88 °C ($CHCl_3$—MeOH). Found (%): C, 58.52; H, 5.48; N, 6.37; S, 14.71. $C_{21}H_{24}N_2O_4S_2$. Calculated (%): C, 58.31; H, 5.59; N, 6.48; S, 14.82. IR, ν/cm^{-1}: 3492, 3388 (NH_2), 2936, 1728 (C=O), 1596, 1548, 1296 (SO_2), 1120 (SO_2), 1100, 1024, 768. ^1H NMR (DMSO-d_6), δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz); 0.87 (t, 3 H, $C\underline{H}_3CH_2O$, J = 7.3 Hz); 1.28—1.37 (m, 2 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.56—1.68 (m, 2 H, $CH_3CH_2C\underline{H}_2CH_2$); 2.62 (s, 3 H, 6-$CH_3$); 3.27 (t, 2 H, CH_3CH_2-$CH_2C\underline{H}_2$, J = 7.3 Hz); 3.96 (q, 2 H, $CH_3C\underline{H}_2O$, J = 7.3 Hz); 5.07 (s, 2 H, NH_2); 7.37—7.46 (m, 2 H, $H_{4\text{-}Ph}(2)$, $H_{4\text{-}Ph}(6)$); 7.52—7.62 (m, 3 H, $H_{4\text{-}Ph}(3)$, $H_{4\text{-}Ph}(4)$, $H_{4\text{-}Ph}(5)$). ^{13}C NMR (DMSO-d_6), δ: 13.34 ($\underline{C}H_3CH_2CH_2CH_2$); 13.39 ($\underline{C}H_3CH_2O$); 20.69 ($CH_3\underline{C}H_2CH_2CH_2$); 22.72 (6-$CH_3$); 24.32 ($CH_3CH_2$-$\underline{C}H_2CH_2$); 55.13 ($CH_3CH_2CH_2\underline{C}H_2$); 61.30 ($CH_3\underline{C}H_2O$); 100.52 ($C_{TP}(2)$); 119.55 ($C_{TP}(3a)$); 126.98 ($C_{TP}(5)$); 128.50 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.68 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 129.68 ($C_{4\text{-}Ph}(4)$); 132.87 ($C_{4\text{-}Ph}(1)$); 144.29 ($C_{TP}(3)$); 144.85 ($C_{TP}(4)$); 155.42 ($C_{TP}(6)$); 160.02 ($C_{TP}(7a)$); 166.63 (C=O).

4,6-Dimethyl-2-(morpholin-4-ylsulfonyl)thieno[2,3-*b*]pyridine-3-amine (3u). The yield was 0.6 g (46%), yellow crystals, m.p. 196—198 °C (MeOH). Found (%): C, 47.78; H, 5.18; N, 12.88; S, 19.50. $C_{13}H_{17}N_3O_3S_2$. Calculated (%): C, 47.69; H, 5.23; N, 12.83; S, 19.58. IR, ν/cm^{-1}: 3419, 3346 (NH_2), 2969, 2862, 1631, 1581, 1449, 1378, 1328 (SO_2), 1264, 1149 (SO_2), 1112, 1069, 938, 793, 726. ^1H NMR (DMSO-d_6), δ: 2.52 (s, 3 H, 4-CH_3); 2.73 (s, 3 H, 6-CH_3); 3.08 (t, 4 H, CH_2NCH_2, J = 4.4 Hz); 3.65 (t, 4 H, CH_2OCH_2, J = 4.4 Hz); 6.05 (s, 2 H, NH_2); 7.12 (s, 1 H, $H_{TP}(5)$). ^{13}C NMR (DMSO-d_6), δ: 19.76 (4-CH_3); 23.77 (6-CH_3); 46.00 (CH_2NCH_2); 65.29 (CH_2OCH_2); 96.01 ($C_{TP}(2)$); 122.42 ($C_{TP}(5)$); 122.53 ($C_{TP}(3a)$); 145.57 ($C_{TP}(3)$); 146.21 ($C_{TP}(4)$); 159.41 ($C_{TP}(7a)$); 159.48 ($C_{TP}(6)$).

2-(Morpholin-4-ylsulfonyl)-4,6-diphenylthieno[2,3-*b*]pyridine-3-amine (3v). The yield was 0.72 g (44%), light yellow crystals, m.p. 204—206 °C ($CHCl_3$—MeOH). Found (%): C, 61.11; H, 4.71; N, 9.34; S, 14.26. $C_{23}H_{21}N_3O_3S_2$. Calculated (%): C, 61.18; H, 4.69; N, 9.31; S, 14.20. IR, ν/cm^{-1}: 3485, 3371 (NH_2), 3061, 1604, 1575, 1535, 1513, 1388, 1328 (SO_2), 1264, 1169, 1145 (SO_2), 1108, 1070, 936, 758, 707. ^1H NMR (DMSO-d_6), δ: 3.14 (t, 4 H, CH_2NCH_2, J = 4.4 Hz); 3.65 (t, 4 H, CH_2OCH_2, J = 4.4 Hz); 5.20 (s, 2 H, NH_2); 7.47—7.55 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 7.57—7.62 (m, 5 H, 4-Ph); 7.83 (s, 1 H, $H_{TP}(5)$);

8.17—8.25 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$). ^{13}C NMR (DMSO-d_6), δ: 46.00 (CH_2NCH_2); 65.31 (CH_2OCH_2); 96.94 ($C_{TP}(2)$); 118.86 ($C_{TP}(5)$); 120.56 ($C_{TP}(3a)$); 127.28 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 128.74 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.87 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 128.94 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$); 129.37 ($C_{4\text{-}Ph}(4)$); 130.11 ($C_{6\text{-}Ph}(4)$); 136.05 ($C_{4\text{-}Ph}(1)$); 137.11 ($C_{6\text{-}Ph}(1)$); 143.97 ($C_{TP}(3)$); 148.42 ($C_{TP}(4)$); 156.25 ($C_{TP}(6)$); 160.27 ($C_{TP}(7a)$).

3-Amino-4,6-dimethyl-*N*-phenylthieno[2,3-*b*]pyridine-2-sulfonamide (3w). The yield was 0.48 g (36%), yellow crystals, m.p. 207—208 °C (MeOH). Found (%): C, 54.11; H, 4.48; N, 12.53; S, 19.35. $C_{15}H_{15}N_3O_2S_2$. Calculated (%): C, 54.03; H, 4.53; N, 12.60; S, 19.23. IR, ν/cm^{-1}: 3508, 3388 (NH_2), 2981, 2751, 2685, 1608, 1548, 1510, 1495, 1317 (SO_2), 1301, 1145 (SO_2), 1116, 1010, 943, 697. ^{1}H NMR (DMSO-d_6), δ: 2.46 (s, 3 H, 4-CH_3); 2.67 (s, 3 H, 6-CH_3); 6.01 (s, 2 H, NH_2); 6.98—7.10 (m, 2 H, $H_{PhN}(4)$, $H_{TP}(5)$); 7.14 (d, 2 H, $H_{PhN}(2)$, $H_{PhN}(6)$, J = 7.3 Hz); 7.24 (t, 2 H, $H_{PhN}(3)$, $H_{PhN}(5)$, J = 7.3 Hz); 10.43 (br.s, 1 H, $NHSO_2$). ^{13}C NMR (DMSO-d_6), δ: 19.71 (4-CH_3); 23.72 (6-CH_3); 100.95 ($C_{TP}(2)$); 119.75 ($C_{PhN}(2)$, $C_{PhN}(6)$); 122.23 ($C_{TP}(5)$); 122.39 ($C_{TP}(3a)$); 123.99 ($C_{PhN}(4)$); 129.13 ($C_{PhN}(3)$, $C_{PhN}(5)$); 137.60 ($C_{PhN}(1)$); 144.68 ($C_{TP}(3)$); 145.29 ($C_{TP}(4)$); 159.16 ($C_{TP}(6)$); 159.22 ($C_{TP}(7a)$).

3-Amino-4,6-diphenyl-*N*-phenylthieno[2,3-*b*]pyridine-2-sulfonamide (3x). The yield was 0.56 g (32%), yellow crystals, m.p. 190—192 °C (MeOH). Found (%): C, 65.51; H, 4.12; N, 9.27; S, 14.08. $C_{25}H_{19}N_3O_2S_2$. Calculated (%): C, 65.62; H, 4.19; N, 9.18; S, 14.01. IR, ν/cm^{-1}: 3499, 3398, 3253 (NH_2), 3058, 1608, 1573, 1536, 1496, 1315 (SO_2), 1299, 1136 (SO_2), 1002, 918, 750, 693. ^{1}H NMR (DMSO-d_6), δ: 5.13 (s, 2 H, NH_2); 7.04 (t, 1 H, $H_{PhN}(4)$, J = 6.6 Hz); 7.15 (d, 2 H, $H_{PhN}(2)$, $H_{PhN}(6)$, J = 7.3 Hz); 7.25 (t, 2 H, $H_{PhN}(3)$, $H_{PhN}(5)$, J = 7.3 Hz); 7.37—7.56 (m, 5 H, 4-Ph); 7.59—7.65 (m, 3 H, $H_{6\text{-}Ph}(3)$, $H_{6\text{-}Ph}(4)$, $H_{6\text{-}Ph}(5)$); 7.76 (s, 1 H, $H_{TP}(5)$); 8.12—8.22 (m, 2 H, $H_{6\text{-}Ph}(2)$, $H_{6\text{-}Ph}(6)$); 10.43 (br.s, 1 H, $NHSO_2$). ^{13}C NMR (DMSO-d_6), δ: 101.73 ($C_{TP}(2)$); 118.76 ($C_{TP}(5)$); 119.98 ($C_{PhN}(2)$, $C_{PhN}(6)$); 120.27 ($C_{TP}(3a)$); 124.13 ($C_{PhN}(4)$); 127.21 ($C_{6\text{-}Ph}(3)$, $C_{6\text{-}Ph}(5)$); 128.67 ($C_{6\text{-}Ph}(2)$, $C_{6\text{-}Ph}(6)$), 128.83 ($C_{4\text{-}Ph}(3)$, $C_{4\text{-}Ph}(5)$); 128.86 ($C_{4\text{-}Ph}(2)$, $C_{4\text{-}Ph}(6)$); 129.13 ($C_{PhN}(3)$, $C_{PhN}(5)$); 129.37 ($C_{4\text{-}Ph}(4)$); 130.02 ($C_{6\text{-}Ph}(4)$); 135.89 ($C_{4\text{-}Ph}(1)$); 137.05 ($C_{6\text{-}Ph}(1)$); 137.47 ($C_{PhN}(1)$); 142.74 ($C_{TP}(3)$); 148.15 ($C_{TP}(4)$); 156.07 ($C_{TP}(6)$); 159.95 ($C_{TP}(7a)$).

4,6-Dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3-oles (6a—e) and 4,6-dimethyl-2-(organylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-ones (7a—e) (general procedure). Anhydrous K_2CO_3 (0.53 g, 4.5 mmol) was added under stirring at 50 °C to a solution of methyl 4,6-dimethylpyridin-2(1*H*)-thione-3-carboxylate **5** (0.59 g, 3 mmol)[11] and chloromethyl organyl sulfone **2a—e** (3 mmol) in DMF (5 mL). The reaction mixture was stirred at 75—80 °C for 50 min, cooled to room temperature, and poured into water (30 mL). The resulting solution was acidified with AcOH, and the product was extracted with $CHCl_3$ (3×15 mL). The extract was washed with H_2O (3×20 mL) and dried over $MgSO_4$, the solvent was evaporated, and the product was purified by chromatography on silica gel. The eluent was $CHCl_3$. The eluate was evaporated, and the product was recrystallized from methanol.

4,6-Dimethyl-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3-ol (6a) and 4,6-dimethyl-2-(phenylsulfonyl)thieno[2,3-*b*]pyridine-3(2*H*)-one (7a) (6a : **7a** = 80 : 20). The yield was 0.49 g (51%), pink crystals, m.p. 143.5—145 °C (MeOH). Found (%): C, 56.57; H, 4.22; N, 4.30; S, 20.15. $C_{15}H_{13}NO_3S_2$. Calculated (%): C, 56.41; H, 4.10; N, 4.39; S, 20.08. IR, ν/cm^{-1}: 3320 (OH), 3064, 2920, 1588, 1560, 1504, 1312 (SO_2), 1192, 1144 (SO_2), 1124, 820, 724, 688. ^{1}H NMR ($CDCl_3$), δ: 2.50 (s, 0.6 H, 4-CH_3, **7a**); 2.52 (s, 0.6 H, 6-CH_3, **7a**); 2.61 (s, 2.4 H, 4-CH_3, **6a**); 2.73 (s, 2.4 H, 6-CH_3, **6a**); 5.21 (s, 0.2 H, $H_{TP}(2)$, **7a**); 6.77 (s, 0.2 H, $H_{TP}(5)$, **7a**); 6.91 (s, 0.8 H, $H_{TP}(5)$, **6a**); 7.50—7.70 (m, 3 H, $H_{PhSO_2}(3)$, $H_{PhSO_2}(4)$, $H_{PhSO_2}(5)$); 7.95 (d, 0.4 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz, **7a**), 8.00 (d, 1.6 H, $H_{PhSO_2}(2)$, $H_{PhSO_2}(6)$, J = 7.3 Hz, **6a**); 9.56 (br.s, 0.8 H, 3-OH, **6a**). ^{13}C NMR (DMSO-d_6), δ: 17.53 (4-CH_3, **7a**); 18.69 (4-CH_3, **6a**); 23.99 (6-CH_3, **6a**); 24.14 (6-CH_3, **7a**); 72.38 ($C_{TP}(2)$, **7a**); 112.24 ($C_{TP}(2)$, **6a**); 120.83 ($C_{TP}(3a)$, **7a**); 122.72 ($C_{TP}(5)$, **6a**, **7a**); 123.68 ($C_{TP}(3a)$, **6a**); 126.82 ($C_{PhSO_2}(3)$, $C_{PhSO_2}(5)$, **6a**, **7a**), 129.32 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$, **7a**), 129.62 ($C_{PhSO_2}(2)$, $C_{PhSO_2}(6)$, **6a**), 133.84 ($C_{PhSO_2}(4)$, **6a**), 134.90 ($C_{PhSO_2}(4)$, **7a**), 141.65 ($C_{PhSO_2}(1)$, **6a**), 142.23 ($C_{PhSO_2}(1)$, **7a**), 146.35 ($C_{TP}(3)$, **6a**); 151.97 ($C_{TP}(4)$, **7a**); 152.27 ($C_{TP}(4)$, **6a**); 158.25 ($C_{TP}(6a)$, **6a**); 160.07 ($C_{TP}(6)$, **6a**); 166.14 ($C_{TP}(6)$, **7a**); 171.32 ($C_{TP}(7a)$, **7a**); 189.15 ($C_{TP}(3)$, **7a**).

2-(Benzylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3-ol (6b) and 2-(benzylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3(2*H*)-one (7b) (6b : **7b** = 68 : 32). The yield was 0.23 g (23%), pink crystals, m.p. 115.5—117 °C (MeOH). Found (%): C, 57.81; H, 4.62; N, 4.38; S, 19.14. $C_{16}H_{15}NO_3S_2$. Calculated (%): C, 57.64; H, 4.53; N, 4.20; S, 19.23. IR, ν/cm^{-1}: 3328 (OH), 3068, 2955, 2916, 1584, 1564, 1508, 1312 (SO_2), 1204, 1152 (SO_2), 1092, 1020, 828, 760, 700. ^{1}H NMR ($CDCl_3$), δ: 2.58 (s, 3 H, 4-CH_3, **6b**, **7b**); 2.62 (s, 0.96 H, 6-CH_3, **7b**); 2.65 (s, 2.04 H, 6-CH_3, **6b**); 4.48 (s, 2 H, CH_2SO_2); 5.06 (s, 0.32 H, $H_{TP}(2)$, **7b**); 6.87 (s, 0.32 H, $H_{TP}(5)$, **7b**); 6.99 (s, 0.68 H, $H_{TP}(5)$, **6b**); 7.20—7.44 (m, 5 H, $CH_2\underline{Ph}$), 8.82 (br.s, 0.68 H, 3-OH, **6b**). ^{13}C NMR (DMSO-d_6), δ: 17.66 (4-CH_3, **7b**); 18.73 (4-CH_3, **6b**); 23.97 (6-CH_3, **6b**); 24.31 (6-CH_3, **7b**); 57.30 (Ph$\underline{C}H_2$, **7b**); 61.45 (Ph$\underline{C}H_2$, **6b**); 69.90 ($C_{TP}(2)$, **7b**); 109.61 ($C_{TP}(2)$, **6b**); 120.82 ($C_{TP}(3a)$, **7b**); 122.54 ($C_{TP}(5)$, **6b**); 123.05 ($C_{TP}(5)$, **7b**); 123.87 ($C_{TP}(3a)$, **6b**); 128.38 ($C_{BnSO_2}(3)$, $C_{BnSO_2}(5)$); 128.70 ($C_{BnSO_2}(4)$); 130.95 ($C_{BnSO_2}(2)$, $C_{BnSO_2}(6)$); 131.48 ($C_{BnSO_2}(1)$); 146.17 ($C_{TP}(3)$, **6b**); 151.87 ($C_{TP}(4)$, **7b**); 152.42 ($C_{TP}(4)$, **6b**); 158.32 ($C_{TP}(7a)$, **6b**); 159.91 ($C_{TP}(6)$, **6b**); 166.37 ($C_{TP}(6)$, **7b**); 171.76 ($C_{TP}(7a)$, **7b**); 189.68 (C(3), **7b**).

2-(Butylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3-ol (6c) and 2-(butylsulfonyl)-4,6-dimethylthieno[2,3-*b*]pyridine-3(2*H*)-one (7c) (6c : **7c** = 83 : 17). The yield was 0.37 g (41%), pink crystals, m.p. 60—62 °C (MeOH). Found (%): C, 52.35; H, 5.88; N, 4.55; S, 21.64. $C_{13}H_{17}NO_3S_2$. Calculated (%): C, 52.15; H, 5.72; N, 4.68; S, 21.42. IR, ν/cm^{-1}: 3396 (OH), 2970, 2956, 2928, 2870, 1707 (C=O), 1587, 1564, 1509, 1312 (SO_2), 1242, 1192, 1140 (SO_2), 1094, 1023, 820, 764, 764, 651. ^{1}H NMR ($CDCl_3$), δ: 0.95 (t, 2.5 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz, **6c**); 1.02 (t, 0.5 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 7.3 Hz, **7c**); 1.40—1.54 (m, 1.66 H, $CH_3C\underline{H}_2CH_2CH_2$, **6c**); 1.54—1.61 (m, 0.34 H, $CH_3C\underline{H}_2CH_2CH_2$, **7c**); 1.76—1.86 (m, 1.66 H, $CH_3CH_2C\underline{H}_2CH_2$, **6c**); 1.90—2.01 (m, 0.34 H, $CH_3CH_2C\underline{H}_2CH_2$, **7c**); 2.59 (s, 0.5 H, 4-CH_3, **7c**); 2.60 (s, 0.5 H, 6-CH_3, **7c**); 2.67 (s, 2.5 H, 4-CH_3, **6c**); 2.75 (s, 2.5 H, 6-CH_3, **6c**); 3.29 (t, 1.66 H, $CH_3CH_2CH_2\underline{C}H_2$, J = 8.1 Hz, **6c**); 3.43 (t.d, 0.34 H, $CH_3CH_2CH_2\underline{C}H_2$, J_1 = 8.1 Hz, J_2 = 2.9 Hz, **7c**); 5.16 (s, 0.17 H, $H_{TP}(2)$, **7c**); 6.88 (s, 0.17 H, $H_{TP}(5)$, **7c**); 7.05 (s, 0.83 H, $H_{TP}(5)$, **6c**); 9.44 (br.s, 0.83 H, 3-OH, **6c**). ^{13}C NMR (DMSO-d_6), δ: 13.37 ($\underline{C}H_3CH_2CH_2CH_2$); 17.56 (4-$CH_3$, **7c**); 18.66 (4-$CH_3$, **6c**); 20.72 ($CH_3\underline{C}H_2CH_2CH_2$, **6c**); 21.00 ($CH_3\underline{C}H_2CH_2CH_2$, **7c**); 22.84 ($CH_3CH_2\underline{C}H_2CH_2$, **7c**); 23.91 (6-$CH_3$, **6c**); 24.27 (6-$CH_3$, **7c**); 24.34 ($CH_3CH_2\underline{C}H_2CH_2$, **6c**); 50.92 ($CH_3CH_2CH_2\underline{C}H_2$, **7c**); 55.46 ($CH_3CH_2CH_2\underline{C}H_2$, **6c**); 70.18 ($C_{TP}(2)$, **7c**); 110.45 ($C_{TP}(2)$, **6c**); 119.67 ($C_{TP}(3a)$, **7c**); 122.53 ($C_{TP}(5)$, **6c**); 122.83 ($C_{TP}(3a)$, **6c**); 122.97 ($C_{TP}(5)$, **7c**); 146.12 ($C_{TP}(3)$, **6c**); 151.32 ($C_{TP}(4)$, **7c**); 151.88

(C_{TP}(4), **6c**); 158.02 (C_{TP}(7a), **6c**); 159.90 (C_{TP}(6), **6c**); 166.34 (C_{TP}(6), **7c**); 172.20 (C_{TP}(7a), **7c**); 190.67 (C_{TP}(3), **7c**).

4,6-Dimethyl-2-(morpholin-4-ylsulfonyl)thieno[2,3-*b*]pyridine-3-ol (6d) and 4,6-dimethyl-2-(morpholin-4-ylsulfonyl)-thieno[2,3-*b*]pyridin-3(2*H*)-one (7d) (6d : **7d** = 90 : 10). The yield was 0.43 g (43%), pink crystals, m.p. 148—150 °C (MeOH). Found (%): C, 47.37; H, 5.02; N, 8.41; S, 19.61. $C_{13}H_{16}N_2O_4S_2$. Calculated (%): C, 47.55; H, 4.91; N, 8.53; S, 19.52. IR, ν/cm^{-1}: 3337 (OH), 2967, 2924, 2856, 1704 (C=O), 1587, 1567, 1509, 1449, 1346, 1331 (SO_2), 1262, 1199, 1153 (SO_2), 1070, 1017, 939, 820, 727. ^{1}H NMR ($CDCl_3$), δ: 2.59 (s, 0.3 H, 4-CH_3, **7d**); 2.60 (s, 0.3 H, 6-CH_3, **7d**); 2.65 (s, 2.7 H, 4-CH_3, **6d**); 2.73 (s, 2.7 H, 6-CH_3, **6d**); 3.23 (t, 3.6 H, CH_2NCH_2, *J* = 4.4 Hz, **6d**); 3.43—3.53 (m, 0.4 H, CH_2NCH_2, **7d**); 3.63—3.70 (m, 0.4 H, CH_2OCH_2, **7d**); 3.80 (t, 3.6 H, CH_2OCH_2, *J* = 4.4 Hz, **6d**); 5.17 (s, 0.1 H, H_{TP}(2), **7d**); 6.88 (s, 0.1 H, H_{TP}(5), **7d**); 7.03 (s, 0.9 H, H_{TP}(5), **6d**); 9.01 (br.s, 0.9 H, 3-OH, **6d**). ^{13}C NMR (DMSO-d_6), δ: 17.59 (4-CH_3, **7d**); 18.72 (4-CH_3, **6d**); 23.91 (6-CH_3, **6d**); 24.27 (6-CH_3, **7d**); 45.92 (CH_2NCH_2, **6d**); 46.62 (CH_2NCH_2, **7d**); 65.27 (CH_2OCH_2, **6d**); 66.05 (CH_2OCH_2, **7d**); 69.45 (C_{TP}(2), **7d**); 105.70 (C_{TP}(2), **6d**); 120.04 (C_{TP}(3a), **7d**); 122.47 (C_{TP}(5), **7d**); 122.58 (C_{TP}(5), **6d**); 122.90 (C_{TP}(3a), **6d**); 145.98 (C_{TP}(3), **6d**); 151.77 (C_{TP}(4), **6d**); 151.87 (C_{TP}(4), **7d**); 157.39 (C_{TP}(7a), **6d**); 159.78 (C_{TP}(6), **6d**); 166.27 (C_{TP}(6), **7d**); 171.93 (C_{TP}(7a), **7d**); 190.14 (C_{TP}(3), **7d**).

3-Hydroxy-4,6-dimethyl-*N*-phenylthieno[2,3-*b*]pyridine-2-sulfonamide (6e) and 4,6-dimethyl-3-oxo-*N*-phenyl-2,3-dihydrothieno[2,3-*b*]pyridine-2-sulfonamide (7e) (6e : **7e** = 40 : 60). The yield was 0.48 g (48%), light porcelain crystals, m.p. 182—184 °C (MeOH). Found (%): C, 54.06; H, 4.31; N, 8.21; S, 19.29. $C_{15}H_{14}N_2O_3S_2$. Calculated (%): C, 53.88; H, 4.22; N, 8.38; S, 19.17. IR, ν/cm^{-1}: 3455 (NH), 3294 (OH), 3012, 2868, 2800, 2697, 1728 (C=O), 1592, 1584, 1516, 1493, 1318 (SO_2), 1222, 1202, 1142 (SO_2), 1114, 1015, 943, 819, 755, 696, 647, 592. ^{1}H NMR ($CDCl_3$), δ: 2.58 (s, 3.6 H, 4,6-CH_3, **7e**); 2.63 (s, 1.2 H, 4-CH_3, **6e**); 2.65 (s, 1.2 H, 6-CH_3, **6e**); 5.07 (s, 0.6 H, H_{TP}(2), **7e**); 6.87 (s, 0.6 H, H_{TP}(5), **7e**); 6.98 (s, 0.4H, H_{TP}(5), **6e**); 7.10—7.21 (m, 2 H, H_{PhN}(2), H_{PhN}(6)); 7.24—7.31 (m, 2 H, NH and H_{PhN}(4)); 7.36—7.50 (m, 2 H, H_{PhN}(3), H_{PhN}(5)); 8.90 (br.s, 0.4 H, 3-OH, **6e**). ^{13}C NMR (DMSO-d_6), δ: 17.47 (4-CH_3, **7e**); 18.63 (4-CH_3, **6e**); 23.87 (6-CH_3, **6e**); 24.25 (6-CH_3, **7e**); 69.21 (C_{TP}(2), **7e**); 109.47 (C_{TP}(2), **6e**); 119.61 (C_{TP}(3a), **7e**); 120.19 (C_{PhN}(2), C_{PhN}(6), **6e**); 120.90 (C_{PhN}(2), C_{PhN}(6), **7e**); 122.04 (C_{TP}(3a), **6e**); 122.46 (C_{TP}(5), **6e**); 122.71 (C_{TP}(5), **7e**); 124.48 (C_{PhN}(4), **6e**); 124.65 (C_{PhN}(4), **7e**); 129.08 (C_{PhN}(3), C_{PhN}(5), **7e**); 129.22 (C_{PhN}(3), C_{PhN}(5), **6e**); 136.85 (C_{PhN}(1), **6e**); 137.13 (C_{PhN}(1), **7e**); 145.80 (C_{TP}(3), **6e**); 150.82 (C_{TP}(4), **7e**); 151.11 (C_{TP}(4), **6e**); 157.39 (C_{TP}(7a), **6e**); 159.65 (C_{TP}(6), **6e**); 165.89 (C_{TP}(6), **7e**); 171.52 (C_{TP}(7a), **7e**); 189.14 (C_{TP}(3), **7e**).

The reaction of 4,6-dimethyl-3-cyanopyridine-2-thione (1a) with chloromethyl organyl sulfones 2a,b using sodium methoxide as the base. Sodium methoxide (320 mg, 5.7 mmol) was added to a solution of pyridinethione **1a** (0.82 g, 5 mmol) and chloromethyl phenyl sulfone **2a** (0.95 g, 5 mmol) in anhydrous DMF (12 mL). The reaction mixture was heated at 120—125 °C for 2 h, cooled to room temperature, and diluted with CH_2Cl_2 (30 mL). The resulting solution was filtered from resinous substances, washed with H_2O (3×30 mL), and dried over $MgSO_4$. The solvent was evaporated, and the products were isolated by chromatography on silica gel. The eluent was hexane—$CHCl_3$ mixture (2 : 1 and 3 : 2). The evaporation of fractions gave initial sulfone **2a** (0.46 g, 2.41 mmol) and 4,6-dimethyl-2-{[(phenylsulfonyl)methyl]thio}pyridine-3-carbonitrile **8a** (0.38 g, 1.2 mmol), colorless crystals, m.p. 158—160 °C (MeOH). Found (%): C, 56.67; H, 4.48; N, 8.75; S, 20.05. $C_{15}H_{14}N_2O_2S_2$. Calculated (%): C, 56.58; H, 4.43; N, 8.80; S, 20.14. IR, ν/cm^{-1}: 3062, 2998, 2927, 2218 (CN), 1585, 1543, 1448, 1305 (SO_2), 1271, 1152 (SO_2), 1083, 871, 771, 719, 701, 580. ^{1}H NMR ($CDCl_3$), δ: 2.41 (s, 3 H, 4-CH_3); 2.43 (s, 3 H, 6-CH_3); 5.04 (s, 2 H, SCH_2SO_2); 6.79 (s, 1 H, H_{Py}(5)); 7.42—7.58 (m, 3 H, H_{PhSO_2}(3), H_{PhSO_2}(4), H_{PhSO_2}(5) Ph); 7.70—7.80 (m, 2 H, H_{PhSO_2}(2), H_{PhSO_2}(6)). ^{13}C NMR (DMSO-d_6), δ: 19.45 (4-CH_3); 23.94 (6-CH_3); 51.17 (SCH_2SO_2); 104.49 (C_{Py}(3)); 114.36 (CN); 121.54 (C_{Py}(5)); 128.55 (C_{PhSO_2}(3), C_{PhSO_2}(5)); 128.81 (C_{PhSO_2}(2), C_{PhSO_2}(6)); 134.01 (C_{PhSO_2}(4)); 137.18 (C_{PhSO_2}(1)); 152.77 (C_{Py}(4)); 155.36 (C_{Py}(2)); 161.27 (C_{Py}(6)).

The similar reaction of pyridinthione **1a** (0.66 g, 4 mmol) and chloromethyl benzyl sulfone **2b** (0.82 g, 4 mmol) with sodium methoxide (0.25 mg, 4.6 mmol) in anhydrous DMF (10 mL) gave a mixture of initial sulfone **2b** (0.33 g, 1.61 mmol) and 2-{[(benzylsulfonyl)methyl]thio}-4,6-dimethylpyridine-3-carbonitrile **8b** (0.47 g, 1.41 mmol), colorless crystals, m.p. 150—152 °C (MeOH). Found (%): C, 57.73; H, 4.91; N, 8.35; S, 19.22. $C_{16}H_{16}N_2O_2S_2$. Calculated (%): C, 57.81; H, 4.85; N, 8.43; S, 19.29. IR, ν/cm^{-1}: 2996, 2918, 2216 (CN), 1583, 1356, 1302 (SO_2), 1122 (SO_2), 776, 693. ^{1}H NMR ($CDCl_3$), δ: 2.51 (s, 3 H, 4-CH_3); 2.53 (s, 3 H, 6-CH_3); 4.41 (s, 2 H, Ph$\underline{C}H_2$); 4.81 (s, 2 H, SCH_2SO_2); 6.94 (s, 1 H, H_{Py}(5)); 7.38—7.46 (m, 5 H, Ph). ^{13}C NMR (DMSO-d_6), δ: 19.62 (4-CH_3); 24.09 (6-CH_3); 48.00 (Ph$\underline{C}H_2$); 57.39 (SCH_2SO_2); 104.53 (C_{Py}(3)); 114.56 (CN); 121.73 (C_{Py}(5)); 127.91 (C_{BnSO_2}(1)); 128.47 (C_{BnSO_2}(3), C_{BnSO_2}(4), C_{BnSO_2}(5)); 131.11 (C_{BnSO_2}(2), C_{BnSO_2}(6)); 153.12 (C_{Py}(4)); 156.10 (C_{Py}(2)); 161.51 (C_{Py}(6)).

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